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Applications of free-electron lasers to measurements of
energy transfer in biopolymers and materials

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ABSTRACT

Free-electron lasers (FELs) provide tunable, pulsed radiation in the infrared. Using the FEL as a pump beam, we are investigating the mechanisms for energy transfer between localized vibrational modes and between vibrational modes and lattice or phonon modes. Either a laser-Raman system or a Fourier transform infrared (FTIR) spectrometer will serve as the probe beam, with the attribute of placing the burden of detection on two conventional spectroscopic techniques that circumvent the limited response of infrared detectors. More specifically, the Raman effect inelastically shifts an exciting laser line, typically a visible frequency, by the energy of the vibrational mode; however, the shifted Raman lines also lie in the visible, allowing for detection with highly efficient visible detectors. With regards to FTIR spectroscopy, the multiplex advantage yields a distinct benefit for infrared detector response.

Our group is investigating intramolecular and intermolecular energy transfer processes in both biopolymers and more traditional materials. For example, alkali halides contain a number of defect types that effectively transfer energy in an intermolecular process. Similarly, the functioning of biopolymers depends on efficient intramolecular energy transfer. Understanding these mechanisms will enhance our ability to modify biopolymers and materials with applications to biology, medicine, and materials science.

1. INTRODUCTION

Vanderbilt University has recently constructed a multidisciplinary research center to investigate the applications of FELs to medical and materials research.¹ The FEL was commissioned during the summer of 1991 and now serves as a national facility offering unique opportunities for scientific research. In the past, scientists working with FELs have been specifically concerned with FEL technology development;² after all, a stable and reliable radiation source is required for applications research. FELs are on the verge of achieving both stability and reliability³ and many scientists working with FELs are now concerned with applications of these tunable, pulsed infrared sources with high output power.

In the following we outline the operating characteristics of the Sierra Laser Systems model FEL I and briefly describe the Vanderbilt FEL Center. The FEL is then assessed as a pulsed infrared radiation source for spectroscopic research, two specific FEL applications are described and then discussed as novel spectroscopic techniques for materials and biopolymer research. We conclude with a brief description of future FEL applications currently planned for development at Vanderbilt.

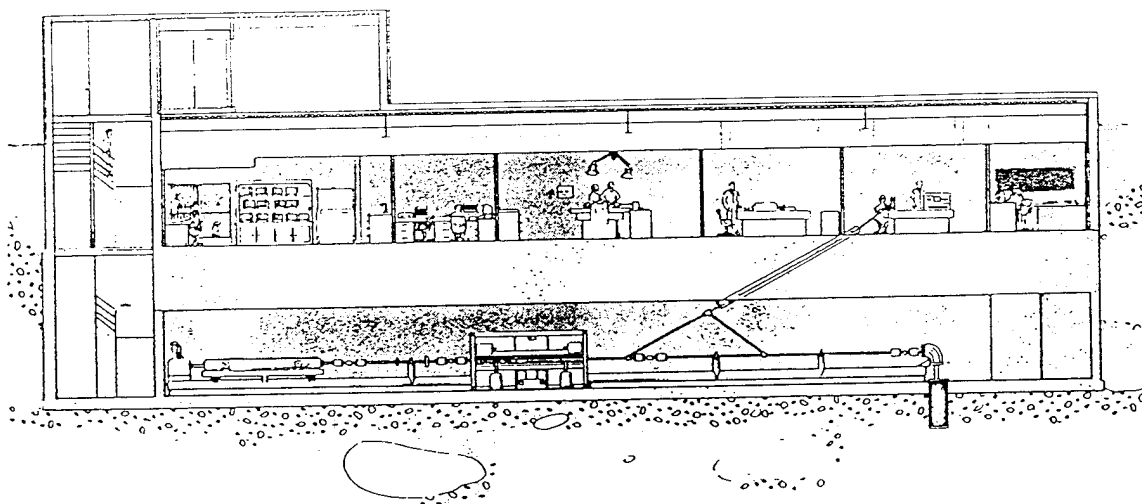


Figure One: Side-View of FEL Facility

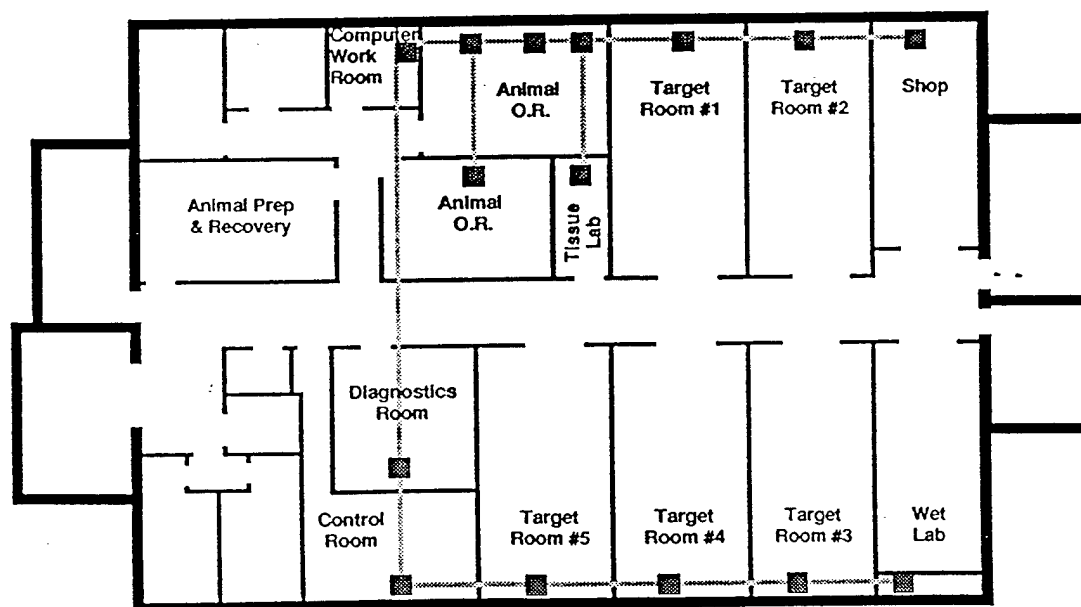


Figure Two: Laboratory Level

Table I: Parameters of the Vanderbilt Free Electron Laser

| | Nominal | Measured |
|-----------------------------|-----------------------------|-----------------------|
| Accelerator | | |
| Electron energy | 20-45 MeV | 36-43 MeV |
| Micropulse peak current | 20-40 A | |
| Macropulse average current | 200 mA | 250 mA |
| Energy spread | 0.5% | 0.5% |
| Normalized emittance | $4\pi \times 10\pi$ mm-mrad | |
| Wiggler | | |
| Wiggler length | 108 cm | 108 cm |
| Wiggler period | 2.3 cm | 2.3 cm |
| Maximum wiggler field (rms) | 0.47 T | 0.44 T |
| Laser | | |
| Wavelength | 2-10 μm | 2.7-4.9 μm |
| Micropulse duration | 0.5-3 ps | |
| Micropulse repetition rate | 2.9 GHz | 2.9 Ghz |
| Macropulse duration | 0.5-6 μs | 6 μs |
| Macropulse energy | 100 mJ | 360 mJ |
| Macropulse repetition rate | 0-60 Hz | 1-30 Hz |
| Overall average power | 0-6 W | 0-11 W |

2. VANDERBILT UNIVERSITY FREE-ELECTRON LASER CENTER

The FEL Center is an operational, state-of-the-art research facility offering a stimulating and diverse environment for scientific research. Figures one and two have been included to give the reader a sense of the scale of the FEL facility. As shown in these figures, the FEL is housed in a vault located below the laboratory level. The FEL control and diagnostics rooms and approximately 6000 square feet of laboratory space, including five target rooms, are located on the laboratory level, as shown in figure two. The FEL Center is located on the main campus, very close to the School of Medicine, the Departments of Physics and Astronomy, Chemistry, and Molecular Biology, and the School of Engineering. The Vanderbilt FEL is a Sierra Laser Systems model FEL I, similar in design to the Stanford Mark III FEL,⁴ providing continuously tunable, pulsed radiation from 2 to 10 microns with both high average and high peak power. The operating parameters are summarized in Table I.

The Vanderbilt Center is the first FEL facility dedicated to applications research. Applications programs in surface physics, materials science, biological physics, molecular biology and biochemistry, biomedical engineering, neurosurgery, head and neck surgery, and radiology have been active since 1987. A large amount of equipment is available for applications research, including ultra-high vacuum chambers, nanosecond and picosecond pulsed-lasers, a laser-Raman system, a Fourier Transform Infrared (FTIR) spectrometer, and a frequency-domain fluorometer. In addition, the Center has well-equipped supporting laboratories for preparing samples for materials and biophysical research and for preparing specimens for biological and medical investigations.

3. APPLICATIONS FOR MATERIALS AND BIOPOLYMERS

During the past several years we have been planning the initial phase of FEL application experiments. One of the first stages in the planning exercise was an assessment, outlined in subsection 3.1, of the infrared FEL as a spectroscopic tool. This assessment indicated that a prudent scientific approach is based on two-color experiments, described in subsection 3.2, using the FEL as the pump beam with more proven spectroscopic techniques serving as the probe beam. We conclude this section with an outline of the scientific issues in materials science (subsection 3.3) and biological physics (subsection 3.4) to be investigated with these techniques.

3.1. Initial considerations for FEL applications research

What non-trivial investigations are appropriate for the initial phase of FEL-application experiments? This question needs to be considered from several points of view. One point of view recognizes the FEL as a novel source of infrared radiation offering continuous tunability over a wide frequency range and delivering pulsed radiation with both high-peak and high-average power. A class of spectroscopic experiments that were impossible a decade ago can now be undertaken: this implies a wealth of experimental opportunity. Another point of view draws the unavoidable comparison to the field of visible spectroscopy, which has enjoyed considerable scientific progress in part due to both the high-Q of visible lasers and to the sensitivity of visible detectors. The performance of infrared detectors does not match that of visible detectors; this wavelength dependence is a fundamental limitation.⁵ Similarly, the power density depends on the ability to focus the laser beam; with regards to infrared investigations of certain non-linear effects an infrared beam does not compare favorably with a visible beam. A third

point of view recognizes the FEL as new technology and at this time it must be regarded as an unproven spectroscopic tool.

After considering the attributes, limitations, and cautionary notes listed in the preceding paragraph, we feel the most prudent phase-one FEL applications should utilize the unique capabilities of the FEL, place the burden of detection on proven spectroscopic techniques, and not place excessive demands on the reliability and stability of the FEL. Two-color experiments meet these guidelines and two examples are described in the following subsections.

3.2. Two-color FEL applications

Recognizing the considerations presented in subsection 3.1, we have configured the FEL as a "pump" beam and two proven, conventional spectroscopic techniques as possible "probe" beams. The fundamental limitation of infrared detectors has been circumvented; the pump-probe schemes to be outlined below can be viewed as replacing the infrared detector with either a Raman or FTIR spectrometer. Our experiments both take advantage of the unique tunability of the infrared FEL beam and the experimental design is such that it does not place heavy demands on FEL performance.

Using two-color techniques, we are investigating the vibrational dynamics of materials and biopolymers with three experimental designs: hole burning measurements using both laser-Raman and FTIR spectrometers as probes to set experimental limits on the lifetime and anharmonicity of vibrational modes and anti-Stokes Raman experiments to measure intermolecular and intramolecular energy transfer.

3.2.1. Applications based on laser-Raman spectroscopy

The first class of two-color experiments uses a laser-Raman spectroscopic system as the probe beam. The Raman effect is due to inelastic scattering of light where the Stokes and anti-Stokes features correspond to phonon creation and annihilation, respectively. If the ratio of transition energy over thermal energy is sufficiently large, the "oscillator" will be in the ground state, phonons will not exist to be annihilated, and thus there will be no thermal contribution to the anti-Stokes spectrum. More specifically, the ratio of the anti-Stokes to Stokes scattering intensity is given by:

$$\frac{I_{AS}}{I_S} = \left[\frac{\nu_o + \nu}{\nu_o - \nu} \right] \frac{e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}$$

where ν_o is the transition frequency and ν is the excitation frequency of the probe laser. For example, at room temperature a vibrational transition at 1000 cm^{-1} probed with a visible excitation frequency of 514 nm has an anti-Stokes to Stokes intensity ratio of 0.01. Thus under appropriate conditions anti-Stokes Raman spectroscopy can serve as a probe for nonequilibrium contributions to vibrational energy levels.

For our experimental setup the FEL is tuned to and "pumps" an infrared-active mode of the system. This results in a non-equilibrium energy distribution, i.e. a "hot" mode that in general couples to other modes with varying efficiencies rendering a distribution of athermally populated modes. A second, visible beam from a conventional laser scatters from this excited system and the scattered light is

collected and focused on the input slit of a double monochromator, effectively probing the occupation numbers of Raman-active vibrational modes. With regards to choice of conventional lasers, experiments using a cw laser identify pathways for energy transfer; experiments using a picosecond pulsed laser will establish rates of energy transfer.

Laser-Raman spectroscopy has added advantages for biological physics. The chronic problem of strongly absorbing water bands in the infrared is avoided since water is relatively transparent in the visible range. Furthermore, in many cases sensitive visible array detectors can be used avoiding the tediously long measurements typical of the photon counting mode. To keep experimental run times manageable, however, somewhat concentrated samples may still be required.

3.2.2 Applications based on FTIR spectroscopy

The second class of two-color experiments uses an FTIR spectrometer system as the probe beam. FTIR spectroscopy is based on the Michelson effect and benefits from the multiplex advantage, i.e. frequencies throughout a broad spectral range are measured simultaneously: for sufficient integrated intensity the impact of the relatively poor performance of infrared detectors is significantly reduced. In this class of experiments the FEL is used as the pump beam to "burn holes" in spectral lineshapes. Hole burning is an experimental technique that modifies a normally smooth inhomogeneously broadened absorption line to elucidate approximate homogeneous lineshapes and lifetimes.⁶ Condensed matter is subject to strains, impurities, and other imperfections that effect a distribution of local environments and thus can result in inhomogeneous broadening of spectral lines. The FEL will be used to burn a homogenous line within the inhomogeneous envelope; the homogeneous line corresponds to a subpopulation of absorbers that experience similar local environments. In some cases the hole can be "persistent," i.e. it remains evident after the pump beam is turned off. The resulting hole renders information concerning mode lifetimes and is the basis for models of energy relaxation. Similarly, for modes that share infrared and Raman activity, the FEL can be used to hole burn modes that are probed with a laser-Raman system.

3.3. Investigations in materials science

Our research group is primarily interested in biopolymer physics. It has usually been our experience that the condensed matter literature contains experimental and theoretical accounts that have served as both guidance for our experimental protocols and as points of comparison to our biophysical results. However, in the past experimental investigations at infrared frequencies have been limited by the lack of a tunable infrared source. The continued development of the FEL is removing this limitation; consequently, we now find ourselves with experimental capabilities for which there is a lack of comparable results from more traditional condensed materials. Naturally we view this development as a great scientific opportunity and in response have expanded our research program to include more traditional materials with the goals of providing both fundamental results in condensed matter physics and leading to a more complete understanding of vibrational dynamics in biopolymer systems.

As a general example of an FEL application investigating more conventional condensed materials we outline collaborative projects with Norman Tolk of Vanderbilt University and Enrigue Silberman and Don Henderson from Fisk University. Energy transfer and energy relaxation processes for molecular species isolated in crystals and low-temperature matrices have received significant experimental and

theoretical attention. The vibrational dynamics of impurities isolated in alkali halides have been previously investigated indicating both a fast relaxation between vibrational modes⁷ and the occurrence of persistent holes in inhomogeneously broadened spectral lines.⁸ In addition, more complicated systems have been investigated. For example, matrix isolated 1,2-difluoroethane exhibits persistent holes;⁹ to account for this effect it has been proposed that pumping the system at low power leads to a molecular reorientation within the matrix cage. In the past, experimental progress has been hindered by the requirement that the spectral lines be coincident with existing infrared sources. Using the two-color techniques described above we will take advantage of the tunability of the FEL to further elucidate the mechanisms for energy transfer and relaxation.

3.4. Investigations in biopolymer physics

Nucleic acids and proteins exhibit a number of vibrational modes in the infrared,^{10,11} as listed in Table II. A subset of these modes are known to be sensitive to conformation and have served as structural markers.¹² In addition, specific base sequences alter the local structure in nucleic acids, as do specific amino acid sequences in proteins, possibly serving as a mechanism for nucleic acid-protein recognition.¹³ The consensus picture is that biopolymers are conformationally flexible and under certain conditions exhibit a range of local conformations and local environments. This structural variability suggests the possibility of inhomogeneous broadening of spectral lines.^{6,14} In fact, FTIR measurements have identified an anomalous spectral feature associated with the sugar ring in nucleic acids. It is well known that A-DNA and B-DNA have structurally distinct sugar ring conformations; we have identified this apparently broadened spectral feature as a candidate mode for hole burning experiments and this serves as a first example of a specific FEL application in biopolymer physics.

Any biological relevance for vibrational modes in biopolymers will be crucially dependent on the mode lifetimes.¹⁵ While picosecond CARS measurements have set limits on the low-temperature vibrational lifetimes (picoseconds to 5 nanoseconds) of amino acids and peptides,¹⁶ this technique is insensitive to a set of closely spaced vibrational lines.¹⁷ The FEL provides the opportunity to carry out hole burning experiments with the aim of both establishing improved limits on mode lifetimes and determining the mechanisms for energy relaxation. This serves as a second example of an FEL application in biopolymer physics.

Energy transfer of excited electronic states in biopolymers has been the subject of intense research with a number of experimental and theoretical techniques;¹⁸ however, the limitations of conventional infrared lasers has complicated the investigation of vibrational energy transfer. The FEL overcomes these limitations of conventional infrared sources and as a third example we will consider the role of anti-Stokes Raman spectroscopy for two-color FEL applications. The FEL will pump a specific vibrational mode of the biopolymers into a non-equilibrium energy distribution and the laser-Raman spectroscopic system will probe the transfer of energy to other modes of the system. Probing with a cw laser will identify pathways for energy transfer; probing with a pulsed picosecond laser will establish rates of energy transfer for a given energy cascade.

Table II: Frequency Range of Vibrational Modes in Biopolymers

| Band | Frequency Range | | Assignment |
|----------------|-----------------|-----------|-----------------------|
| | (cm-1) | (microns) | |
| PROTEINS | | | |
| Amide A | 3300 | 3.0 | N-H |
| Amide B | 3100 | 3.3 | N-H (Fermi resonance) |
| Amide I | 1650 | 6.1 | C=O, N-H, C-N |
| Amide II | 1560 | 6.4 | C-N, N-H |
| Amide III | 1300 | 7.7 | C-N, N-H |
| Amide IV | 625 | 16.0 | O=C-N |
| Amide V | 725 | 13.8 | N-H |
| Amide VI | 600 | 16.7 | C=O |
| Amide VII | 200 | 50.0 | C-N |
| NUCLEIC ACIDS | | | |
| Base | 3300-3600 | 2.8-3.0 | N-H |
| Sugar | 3300-3600 | 2.8-3.0 | O-H |
| Base | 3000-3100 | 3.2-3.3 | C-H |
| Sugar | 2800-3000 | 3.3-3.6 | C-H |
| Base | 1600-1750 | 5.7-6.2 | C-O |
| Base | 1550-1650 | 6.1-6.5 | N-H |
| Base | 1450-1550 | 6.5-6.9 | ring |
| Base | 1300-1460 | 6.8-7.7 | C-H |
| Sugar | 1300-1460 | 6.8-7.7 | C-H |
| Base | 1250-1450 | 6.9-8.0 | ring |
| Phosphate | 1225 | 8.2 | PO ₂ |
| Phosphate | 1080-1100 | 9.1-9.3 | PO ₂ |
| Sugar | 850-1100 | 9.1-11.8 | C-O, C-C |
| Phosphate | 780-820 | 12.2-12.8 | PO ₂ |
| Sugar | 780-820 | 12.2-12.8 | C-O, C-C |
| Base | 650-800 | 12.5-15.4 | ring |
| Base and Sugar | 300-650 | 15.4-33.3 | skeletal |
| polymer | 12-200 | 50.0-833 | long wavelength |

4. FUTURE APPLICATIONS OF THE VANDERBILT FEL

Now that we are moving into an FEL era that emphasizes applications research, FEL facilities will need to respond to the somewhat diversified demands of the users community. The staff of the Vanderbilt FEL Center are striving to achieve a highly versatile spectroscopic laboratory for infrared physics with broad applications including physical, chemical, engineering, clinical, and biomedical research. Charles Brau, the Director of the Vanderbilt FEL Center, is pursuing ongoing and planned developments for the FEL which have recently been described in detail;³ for completeness, however, we include a summary of these developments. Vanderbilt has an active developmental program to Compton backscatter FEL laser photons off the FEL's electron beam to achieve tunable X-rays with significant applications for radiology. The Center also plans to develop a tunable far-infrared source, known as a Cerenkov FEL, which will be operated synchronously with the conventional infrared FEL allowing novel two-color FEL applications. For time-resolved spectroscopy and other FEL applications shorter macropulses or even single micropulses may be required. Cavity dumping can produce macropulses of the order of 10 nanosecond duration; single micropulses can be produced when a photoelectric injector or pulse chopper is used in conjunction with cavity dumping. Lasing on the third harmonic of the FEL provides photons with wavelengths to about 1 micron and photons down to the near ultraviolet can be obtained with conventional nonlinear harmonic generation techniques. Three techniques have been identified to produce micropulses with durations less than 2 ps: chirping the electron-beam energy, utilizing the synchrotron instabilities, and implementing nonlinear optical fibers and a dispersive delay line will provide compressed optical pulses throughout the wavelength range provided by the Vanderbilt FEL. The reader should not consider this listing to be all inclusive; novel demands from users will challenge the ingenuity of the of the Vanderbilt FEL community.

5. CONCLUDING REMARKS

We are developing FEL applications to investigate hole burning and energy transfer processes in materials and to apply these experimental techniques and results to characterize similar relaxation processes in biopolymers. It should be emphasized that these materials and biopolymers are not disparate systems linked together by a common need for equipment. Clearly biopolymers have many more internal modes and in nature reside in a more complex "host matrix." However, excited vibrational levels of both biopolymers and materials relax via intermolecular and intramolecular processes for energy transfer: while the detailed mechanisms may be system specific, the systematic investigation of energy transfer is not.

The research program described in this paper is also significant from an instrumental point of view. Both materials and biopolymers exhibit a large number of vibrational modes in the infrared. In the past it has been difficult to achieve coincidence between vibrational eigenfrequencies and the lines of conventional lasers, complicating and to an extent limiting the investigation of hole burning and energy transfer in materials. Current FEL technology overcomes this limitation. We will use the FEL as a tunable pump in the infrared and are interfacing conventional instrumentation, the FTIR and laser-Raman systems, as "probe beams." The FEL will be used to burn infrared-active modes to be probed with FTIR spectroscopy and modes that have mixed infrared and Raman activity to be probed with laser-Raman spectroscopy. Energy transfer will be measured using anti-Stokes Raman spectroscopy. These two-color techniques extend the applications of FEL laser technology in a manner that allows for the utilization of the unique capabilities of the FEL, place the burden of detection on proven

spectroscopic techniques that circumvent the limitations of infrared detectors, and do not place excessive demands on the reliability and stability of the FEL.

6. ACKNOWLEDGMENTS

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